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**(54) PROCESS FOR MAKING ALLOYED STEEL  
 SINTERED PARTS AND SINTER POWDER  
 FOR USE IN THE PROCESS**

(71) We, SINTERMETALLWERK  
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 many, do hereby declare the invention, for  
 which we pray that a patent may be granted  
 to us, and the method by which it is to be  
 performed, to be particularly described in and  
 by the following statement:—

The invention relates to a process for mak-  
 ing homogeneous alloyed steel sintered parts  
 by pressing and sintering a powder mixture  
 containing a hardening alloy and iron powder.

It is known that the mechanical properties,  
 especially the tensile strength of steel sintered  
 parts may be improved by such alloying ele-  
 ments as nickel, copper, chromium, man-  
 ganese and molybdenum. When powders of  
 corresponding compositions are sintered, there  
 will in general be no difficulties when the  
 alloying elements are nickel or copper which  
 have a relatively low affinity for oxygen.  
 When powders containing alloying elements  
 such as manganese are sintered, however,  
 there will be oxidation, with consequent de-  
 grading of the material as a result of heat-  
 ing to the sintering temperature. In the sinter-  
 ing process, not only are some of the oxy-  
 gen-affinitive alloying elements lost by oxida-  
 tion, but also the oxides resulting from this

oxidation impair the diffusion of the alloy  
 ingredients. Further, the resulting oxides,  
 which are present as grain boundary oxides,  
 degrade the dynamic properties of the sintered  
 material.

Sintering is carried out in a reducing or  
 neutral atmosphere in order to prevent oxida-  
 tion. However this will not completely  
 eliminate oxidation of the oxygen affinitive  
 elements, especially manganese, because the  
 furnace atmosphere always retains traces of  
 oxygen, and because the powders being sin-  
 tered always initially contain some oxides and  
 free oxygen. Therefore oxides will be formed  
 during heating to the sintering temperatures,  
 and in the case of manganese, this takes place  
 at relatively low temperatures. To overcome  
 this oxide formation, it is known to sinter  
 in enclosures in the presence of getter sub-  
 stances. This however entails appreciable  
 cost and renders the sintering process of  
 doubtful economic value.

When making alloyed sintered steels, it is  
 also known to make use of alloyed powders  
 prepared by pulverizing a correspondingly  
 alloyed steel melt. While such powders  
 possess the advantage that every powder par-  
 ticle is of the same composition as the finished  
 sintered steel, this is true only if the alloyed

powder is not mixed, before sintering, with iron powder, in order, for instance, to adjust the final composition of the sintered steel or just to dilute the alloy powder. What is more, the use of alloyed powders brings about the drawback that compressibility of the powder mass decreases as the proportion of the alloyed powder initially being sintered increases. Therefore high compressive pressures are required to obtain sufficient density of the sintered product.

Because of the difficulties inherent in using alloyed powders, especially those of relatively brittle steel alloys, in practice the use of mixtures of iron powder and powdered alloy carriers is favoured. Alloy formation then takes place as a result of diffusion during sintering. In the case of such oxygen-affinitive alloying elements as titanium, aluminium and manganese, the selection of the alloy carrier may be of decisive importance. The alloy carrier must meet two requirements: it must possess adequate resistance to oxidation at temperature up to the sintering temperature and it must not adversely affect diffusion of the pertinent alloying elements, so that homogeneous sinter alloys may be produced.

In addition to the poor compressibility of the alloy carriers the large amounts of alloy carriers required to obtain the desired properties in the final sintered product are disadvantageous. A further drawback when using manganese as an alloying element consists in its oxygen affinity being far larger than the oxygen affinity of other alloying ingredients. These drawbacks are the more onerous because manganese provides an appreciably larger increase in the strength of the sintered product than cobalt, chromium and molybdenum, and this increase will be the larger the more homogeneously the manganese is distributed through the sintered product.

According to this invention, a process for making a homogeneous alloyed steel sintered product comprises cold pressing a powder mixture, which contains iron powder and a complex carbide hardening ferro-alloy in powder form containing in solid solution a metallic element which is more oxygen-affinitive than iron, to form a body, and sintering the cold pressed body until the carbide in the body has dissolved.

In this way the oxygen-affinitive element, for example manganese, is protected against oxidation and is released, as are the remaining alloying components, at the sintering temperature which may be, as is conventional, from 1,150 to 12,200°C or above and then diffuse in elemental form until the homogeneous sintered steel alloy is formed.

The invention is based on the appreciation that a number of metallic elements which

are more oxygen-affinitive than iron, such as manganese, may occupy the lattice sites of iron atoms in iron carbide. Thus, carbide forming alloying ingredients such as chromium and molybdenum will be converted into mixed carbides with the iron and these by substitution of the iron atoms then accept metallic elements which are pure oxygen-affinitive than iron such as manganese, aluminium and titanium into the mixed carbides and in so doing protect these alloying elements from oxidation. Because of the relatively high solubility of, for instance, manganese and because of the high oxidation resistance of the complex mixed carbides of iron, chromium, molybdenum, tungsten, and vanadium, the required alloying ingredients may be introduced into the sintered product in this manner without the occurrence of oxidation. The hardening alloy furthermore has the advantage that it is easily compressible which is due to its high proportion of iron. Diffusion of the elemental hardening ingredient into the mixer carbide occurs during sintering, and this ensures the production of a homogeneous steel alloy lacking any heterogeneous precipitation phases. Accordingly, in a sintered steel made by the process of the invention, all of the atoms are in the mixed crystal and the structure lacks any discrete carbides despite the use made of a carbide hardening alloy, as for instance is the case for sintered Stellites (Registered Trade Mark).

Incorporating the manganese or other oxygen-affinitive element into the mixed carbides has the added advantage that the hardness of the carbide hardening alloy will decrease as the content of the element such as manganese increases. The carbide hardening alloy still is brittle enough to allow reduction in size to smallest particles of less than 20 microns, preferably 10 microns.

The invention also consists, according to another of its aspects, in a sinterable hardening alloy when used in the process in accordance with the invention and consisting, by weight, of chromium, in an amount up to 25%, molybdenum in an amount up to 25%, manganese in an amount up to 25% and carbon in an amount up to 10% present as complex carbides, the balance being iron except for impurities, and the manganese being in solution in the carbides. Preferably the hardening alloy powder contains, 15 to 2% chromium, 15 to 20% molybdenum, 15 to 20% manganese, individually or in any combination and 5 to 7% carbon, the balance being iron.

In the process of the present invention the hardening alloy powder is mixed with iron powder, and with compression facilitating constituents and, if appropriate, with graphite to adjust the alloying ingredients to a final composition chromium in an amount

up to 5% molybdenum in an amount up to 5% and manganese in an amount up to 5% each, whether present singly or in combination, and carbon in an amount up to 2%, the balance being iron. Preferably the initial powder is of such composition that the sintered steel will contain, by weight, from 0.4 to 2.0% chromium; 0.4 to 2.0% molybdenum; 0.4 to 2.0% manganese and 0.3 to 1.0% carbon; balance iron.

In addition to the ingredients mentioned, the initial powder may contain one or more additional alloying elements such as copper, nickel, phosphorus, tin, zinc, tungsten, silicon and aluminium, for instance up to 5% copper; up to 5% nickel; up to 0.8% phosphorus; up to 3% tin; up to 3% zinc; up to 2% tungsten; up to 3% silicon and up to 3% aluminium, whether singly or in various combinations.

The invention will be further understood from the description which follows taken in conjunction with the accompanying drawings, in which:—

Figure 1 is a graph showing the dependency of the mechanical properties on the amount of carbide hardening alloy in a powder mixture lacking any free carbon;

Figure 2 is a graph showing the dependency of the mechanical properties on the amount of carbide hardening alloy in a powder mixture containing 0.2% of free carbon;

Figure 3 is a graph showing the dependency of the mechanical properties on the amount of the carbide hardening alloy in a powder mixture containing a total of 0.6% C;

Figure 4 is a graph showing the dependency of the mechanical properties following the two-fold sintering upon the amount of carbide hardening alloy in a powder mixture containing a total of 0.6% C; and

Figure 5 is a graph of the wear and of the strength of various sintered steel.

#### EXAMPLE I

Varying amounts of hardening alloy comprising complex mixed carbides consisting of 20% chromium, 20% molybdenum, 20% manganese and 7% carbon, the remainder being iron, and of a particle size of 10 microns were mixed with an iron powder of a particle size of 80 microns with simultaneous addition of 0.7% Acrawax (Registered Trade Mark), all percentages being weight %, i.e. referenced to the total weight. The powder mixture was compressed into moulded bodies at a pressure of 500 to 600 × 10<sup>3</sup> kg/square metre. The green compacted bodies were sintered for fifty minutes at a temperature of 1,280°C in an atmosphere of dissociated ammonia. The mechanical properties of the sintered steels as a function of proportion by weight of hardening alloys of complex mixed carbides are given by the

graph of Figure 1. It will be seen that an optimum combination of properties is obtained if the proportion of the hardening alloy is from 5 to 7% and if the sintered steel made from this hardening alloy contains, by weight, 1.0 to 1.4% chromium, 1—1.4% molybdenum and 1—1.4% manganese and 0.3 to 0.6% carbon, balance iron.

The density of the sintered steel was 6.6 to 6.9 gm/cubic centimetre.

#### EXAMPLE II

Varying amounts of the hardening alloy powder of Example I, always referred to the total mixture, were mixed with 0.7% Acrawax, 0.2% graphite and the balance iron powder. The powder mixture was sintered under the conditions of Example I, sintered steels with a density of .6 to 6.9 gm/cubic centimetre were obtained. Their mechanical properties are given by the graph of Figure 2.

The graphs of Figure 2 show that optimum combination of properties will be obtained if the addition of hardening alloy from complex mixed carbides amounts, by weight, to 4—5%, or if the sintered steel contains 0.8—1.0% chromium, 0.8—1% molybdenum and 0.8—1% manganese and from 0.5—0.6% carbon, balance iron.

#### EXAMPLE III

Several different amounts of the hardening alloy of Example I and 0.7% of Acrawax referred to the total weight, the balance being powder mixture containing iron were adjusted by addition of graphite to a total content of 0.6% carbon by weight, taking into account the carbon content of the carbide hardening alloy. The individual powder mixtures were compressed and sintered under the conditions of Example I, sintered steels with a density of 6.6 to 6.9 gm/cubic centimetre and with the properties shown in the graph of Figure 3 being obtained.

The shape of the curves in Figure 3 show that an optimum combination of the properties is obtained with an addition, by weight, of 3—5% of hardening alloy, or if there is a sintered steel having the composition, by weight of 0.6—1.0% chromium, 0.6—1.0% molybdenum and 0.6—1.0% manganese and 0.6% C, the balance being iron.

#### EXAMPLE IV

In order to improve further the properties of the sintered steel prepared by the process in accordance with the invention, samples of the highest strength of the sintered steels of Example III containing about 4% of the hardening alloys of complex carbides were austenitized for thirty minutes at 900°C and subsequently quenched in oil and tempered at various temperatures. The temper-



ing temperatures and the corresponding tensile strengths and hardnesses are given in Table I.

TABLE I

| Tempering Temperature °C | Tensile Strength kg/square millimetre | Rockwell Hardness HRC |
|--------------------------|---------------------------------------|-----------------------|
| 200                      | 890                                   | 40                    |
| 300                      | 810                                   | 35                    |
| 400                      | 770                                   | 31                    |

This steel alloy was also subjected, together with three other steels, to a comparative wear test. The results are summarized in the graphs of Figure 5. It was found that the wear resistance of the sintered steel made in accordance with the invention approaches that of the comparison steels.

EXAMPLE V

Powder mixtures corresponding to Example III were compressed at pressures each time of 500—600 × 10<sup>3</sup> kg/square metre. The individual compressed bodies were first presintered under dissociated ammonia gas for thirty minutes at 800°C in a band sintering furnace, were then compressed again at the same pressure and subsequently were finally sintered for fifty minutes at 1,280°C under dissociated ammonia gas. Sintered steels with a density of 6.9 to 7.1 gm/cubic centimetre were obtained, the mechanical properties of which are shown in the graphs of Figure 4.

The shape of the curves of Figure 4 shows that an optimum combination of properties is obtained when from 3 to 5%, by weight,

of a hardening alloy are added, i.e., if the sintered steel contains, by weight, from 0.6 to 1% chromium, 0.6 to 1% molybdenum and 0.6 to 1% manganese, and 0.6% carbon, the balance being iron.

EXAMPLE VI

The alloy of the highest strength from Example V containing about 4% of hardening alloy was hardened and tempered under the conditions of Example IV and with the results listed in Table II:

TABLE II

| Tempering Temperature °C | Tensile Strength kg/square millimetre | Hardness HRC |
|--------------------------|---------------------------------------|--------------|
| 200                      | 940                                   | 45           |
| 300                      | 970                                   | 40           |
| 400                      | 820                                   | 37           |

The data of the above Table show that the tensile strength and hardness of the sintered steels of the invention may be adjusted by heat treatment.

EXAMPLE VII

A powder mixture consisting, by weight, of 4% of the hardening alloy of Example I; 0.3% of graphite and 0.7% of Acrawax, the balance being iron, was compressed at a pressure of 400 kg/square metre into moulded bodies of a density of 6.0 to 6.5 gm/cubic centimetre. The moulded bodies were hot pressed at a temperature of 1,000°C and thereby obtaining a density of 7.5 gm/cubic centimetre or exceeding 7.7 gm/cubic centimetre. The mechanical properties of the sintered steels are set forth in Table III below:

TABLE III

| Density Cubic Centimetre | kg/square millimetre Tensile Strength | kg/square millimetre 0.1 Yield Point | Elongation % | kg/square millimetre E Modulus |
|--------------------------|---------------------------------------|--------------------------------------|--------------|--------------------------------|
| 7.5                      | >850                                  | >620                                 | 8            | 150,000                        |
| >7.7                     | >1,000                                | >700                                 | >9           | 170,000                        |

The sintered steels made by a method in accordance with the invention allow not only heat treatment, but also additional conventional treatment, for instance they may be worked case-hardened, nitrided or blued.

The powder mixture in accordance with the invention may be pressed and sintered in a conventional manner. Moulded bodies may be pressed from the powder mixture at pressures of 400 to 600 kg/square metre and these bodies may then be sintered for about 30 to 60 minutes at from 1,200° to 1,300°C. The moulded bodies also may be presintered for from 20 to 40 minutes at about 800° to 900°C and then be pressed again at a pressure of from 500 to 600 kg/square metre and then sintered finally for from about 30

to 60 minutes at a temperature of 1,200 to 1,300°C. Lastly the moulded bodies may be presintered for from 20 to 40 minutes at 800° to 1,000°C, then hot pressed at a temperature of from 1,000—1,200°C and this may be followed by further sintering for 30 to 60 minutes at 1,200—1,300°C.

We are now aware of Specification No. 1,384,658, in which is claimed:—

A process for the production of sintered steel, comprising the steps of

a) forming a ferroalloy by melting alloy components to form an alloy consisting essentially of:—

- 1 to 15% carbon
- 5 to 30% chromium

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1,504,547

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1 to 35% tungsten, and  
1 to 25% vanadium,

together with one or more of the following elements

5 molybdenum up to 30%  
titanium up to 15%  
tantalum up to 15% and  
niobium up to 15%  
balance iron,

10 b) powdering the said ferro-alloy,  
c) mixing the said powdered ferro-alloy  
with powdered ductile iron, and  
d) compacting and sintering the powdered  
mixture.

15 We make no claim to this invention.  
Subject to the foregoing disclaimer,

#### WHAT WE CLAIM IS:—

20 1 A process for making a homogeneous  
alloyed steel sintered product comprising cold  
pressing a powder mixture, which contains  
iron powder and a complex carbide hardening  
ferro-alloy in powder form containing in solid  
25 solution a metallic element which is more  
oxygen-affinitive than iron, to form a body,  
and sintering the cold pressed body until the  
carbide in the body has dissolved.

2. A process according to claim 1, in which  
the hardening alloy powder contains, by  
weight, chromium in an amount up to 25%,  
30 molybdenum in an amount up to 25%, man-  
ganese as the oxygen-affinitive element in an  
amount up to 25%, and carbon in an amount  
up to 10% present as complex carbides, and  
the balance iron except for impurities.

35 3. A process according to claim 1, in which  
the powder mixture contains, by weight,  
chromium in an amount up to 5%, molyb-  
denum in an amount up to 5%, manganese  
as the oxygen-affinitive element in an amount  
40 up to 5%, carbon in an amount up to 2%  
present as complex carbides, copper in an  
amount up to 5%, nickel in an amount up to  
5%, phosphorus in an amount up to 0.8%,  
tin in an amount up to 3%, tungsten in an  
45 amount up to 2%, silicon in an amount up  
to 3%, aluminium in an amount up to 3%  
and the balance iron except for impurities.

4. A process according to claim 3, in which  
the powder mixture contains, by weight,

from 0.4 to 2.0% chromium, from 0.4 to 2.0% 50  
manganese, from 0.4 to 2.0% molybdenum,  
from 0.3 to 1.0% carbon and the balance  
iron except for impurities.

5. A process according to claim 3, in which  
the powder mixture contains, by weight, 55  
from 1.0 to 1.4% chromium, from 1.0 to  
1.4% manganese, from 1.0 to 1.4% molyb-  
denum and from 0.3 to 0.6% carbon and the  
balance iron except for impurities.

6. A sinterable hardening alloy powder 60  
when used in the process in accordance with  
claim 2, consisting, by weight, of chromium  
in an amount up to 25%, molybdenum in an  
amount up to 25%, manganese in an amount  
up to 25%, carbon in an amount up to 65  
10% present as complex carbides, the balance  
being iron except for impurities, and the  
manganese being in solution in the carbides.

7. A powder mixture when used in the  
process in accordance with claim 3, consist- 70  
ing, by weight, of chromium in an amount  
up to 5%, molybdenum in an amount up to  
5%, manganese in an amount up to 5%,  
carbon in an amount up to 2% present as  
complex carbides, copper in an amount up to  
75 5%, nickel in an amount up to 5%, phos-  
phorus in an amount up to 0.8%, tin in an  
amount up to 3%, tungsten in an amount up  
to 2%, silicon in an amount up to 3%,  
80 aluminium in an amount up to 3% and the  
balance iron except for impurities.

8. A powder mixture according to claim 7,  
consisting, by weight, of 0.4 to 2.0% chro-  
mium, 0.4 to 2.0% manganese, 0.4 to 2.0% 85  
molybdenum, 0.3 to 1.0% carbon present  
as complex carbides, and the balance iron  
except for impurities.

9. A powder mixture according to claim 7,  
consisting, by weight, of 1.0 to 1.4% chro- 90  
mium, 1.0 to 1.4% manganese, 1.0 to 1.4%  
molybdenum and 0.3 to 0.6% carbon present  
as complex carbides and the balance iron  
except for impurities.

10. A process according to claim 1, sub- 95  
stantially as described in any one of Examples  
I to VII and with reference to the accompany-  
ing drawings.

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1504547    COMPLETE SPECIFICATION  
5 SHEETS    This drawing is a reproduction of  
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                 Sheet 1

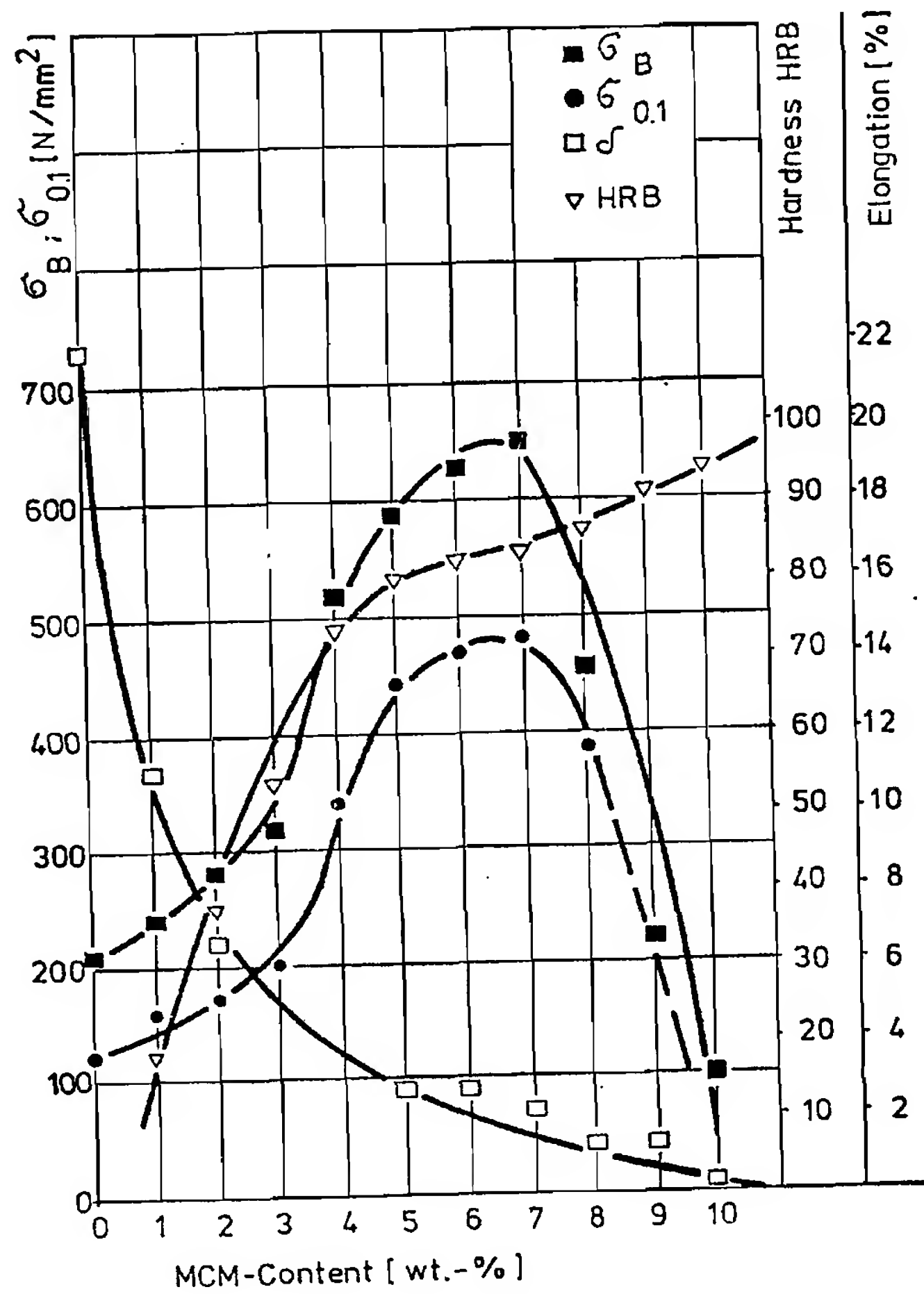


FIG.1

1504547    COMPLETE SPECIFICATION

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Sheet 2

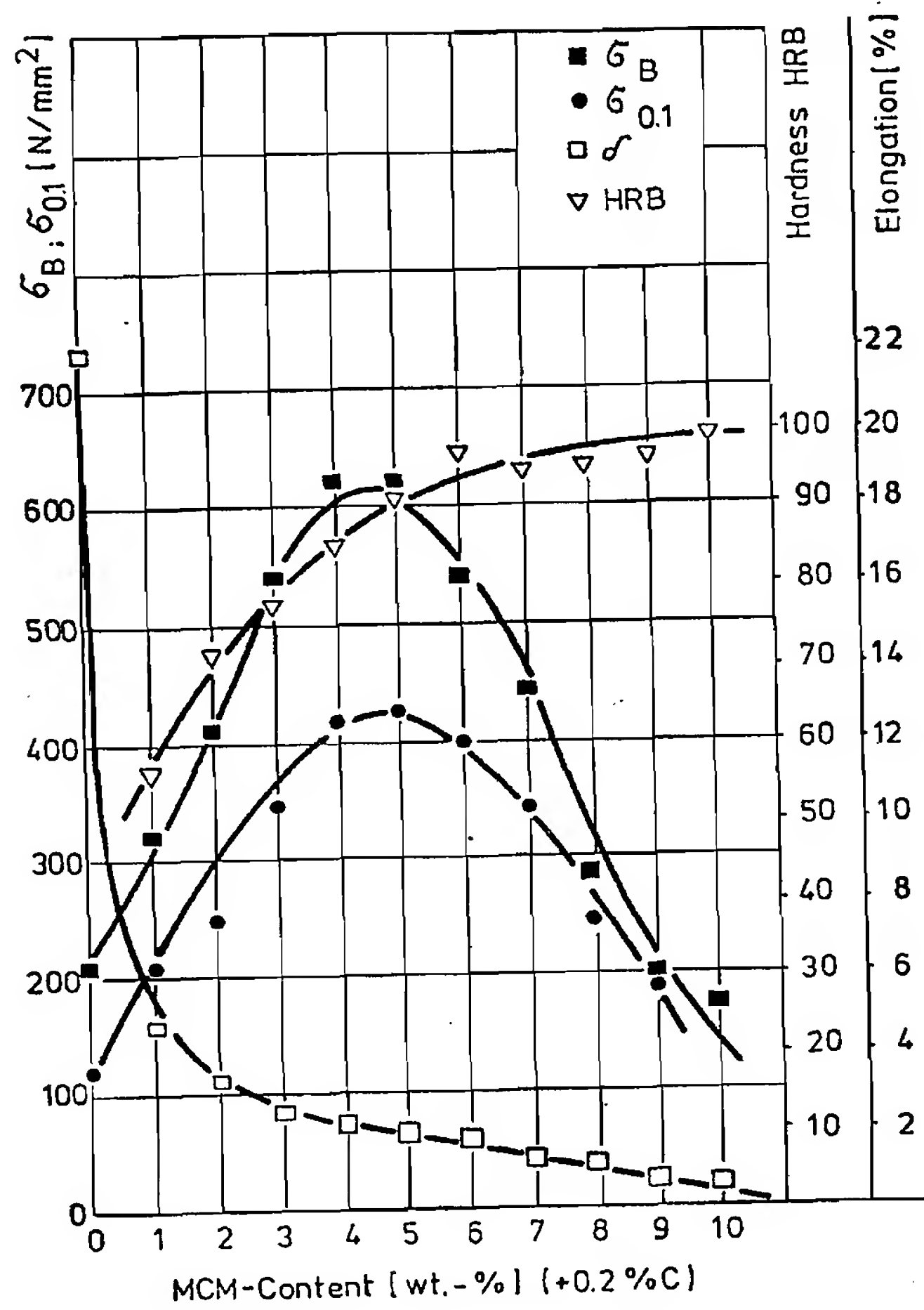


FIG.2

## 1504547 COMPLETE SPECIFICATION

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Sheet 3

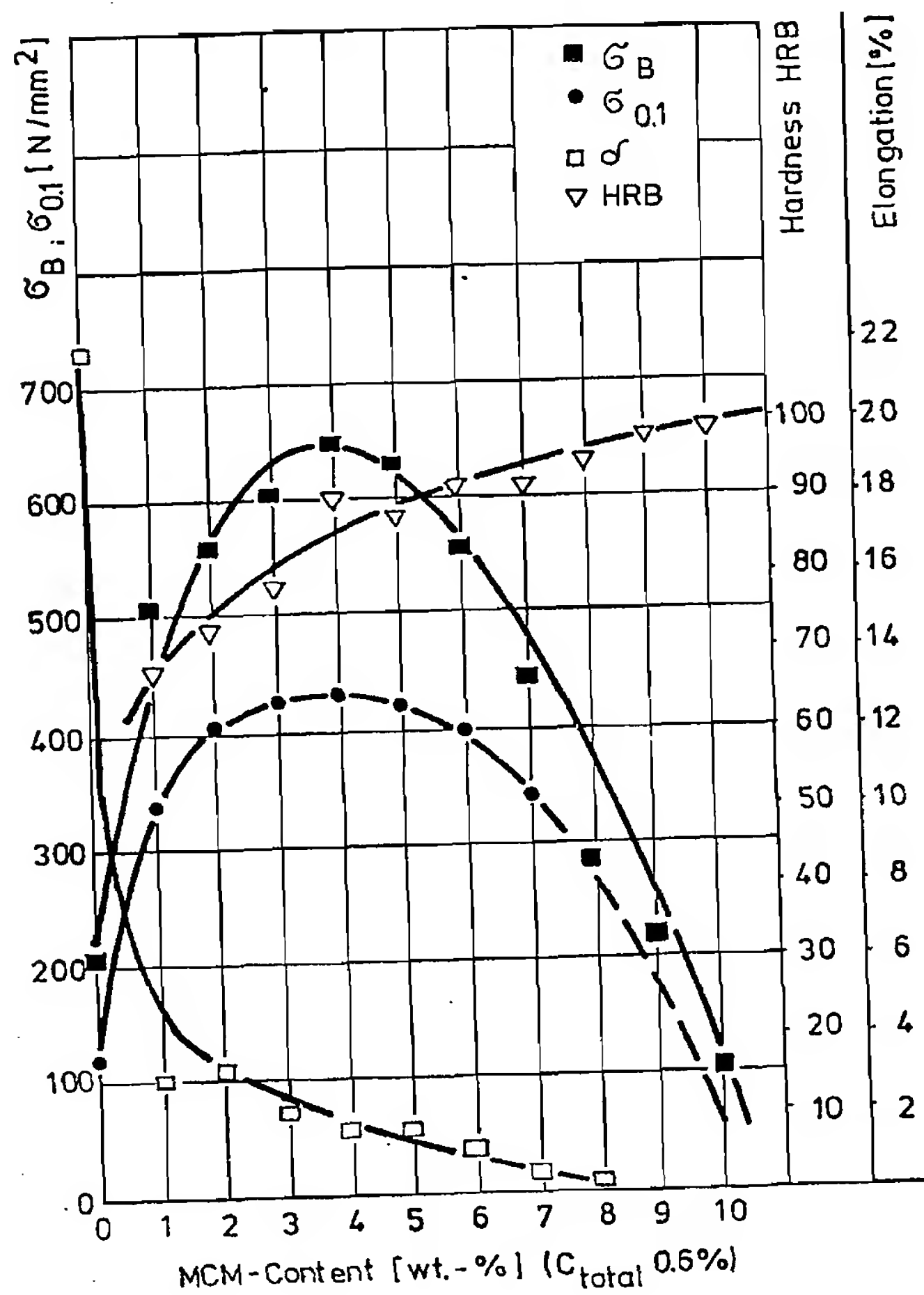


FIG.3



1504547    COMPLETE SPECIFICATION

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Sheet 4

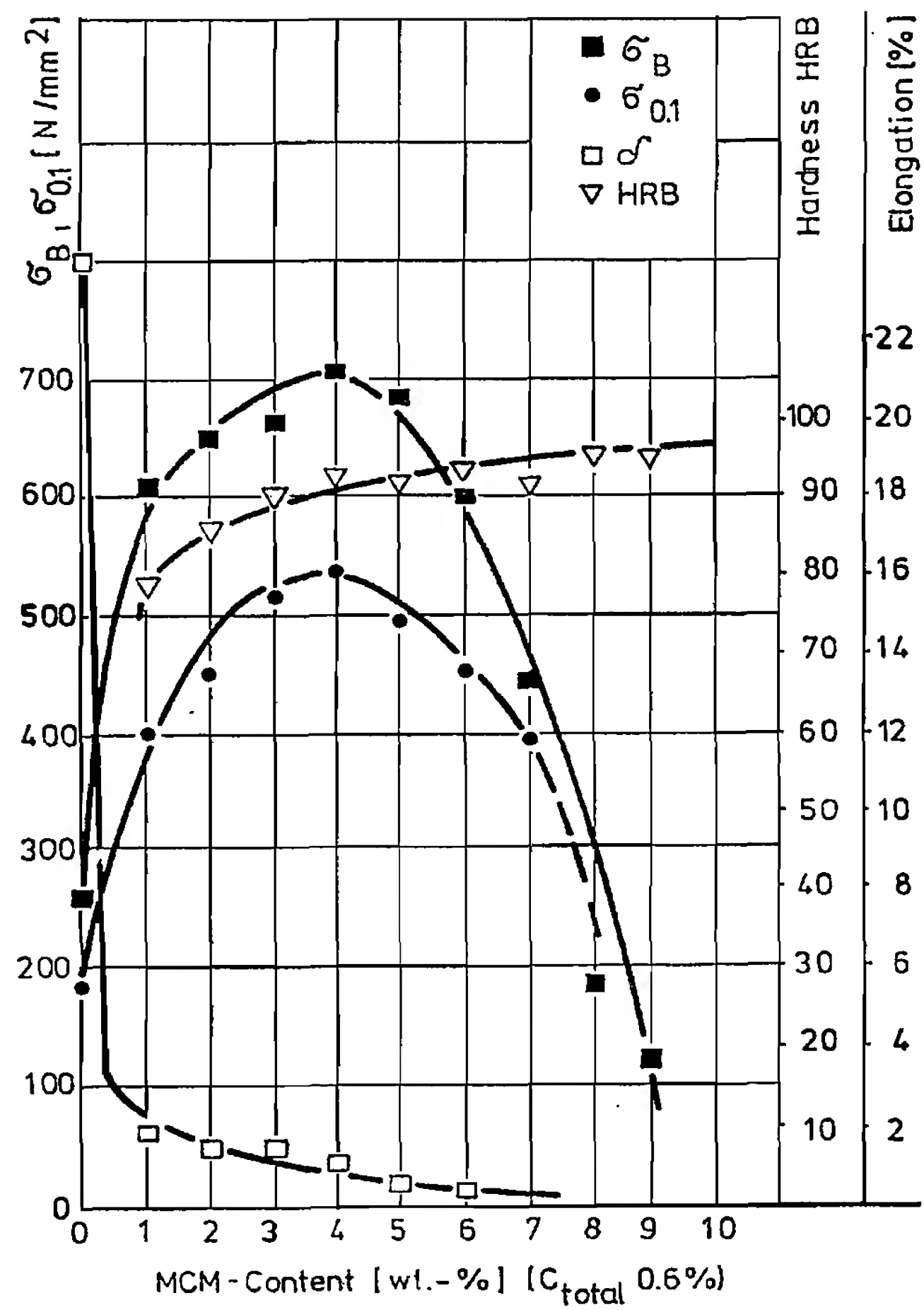


FIG.4

1504547 COMPLETE SPECIFICATION  
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Sheet 5

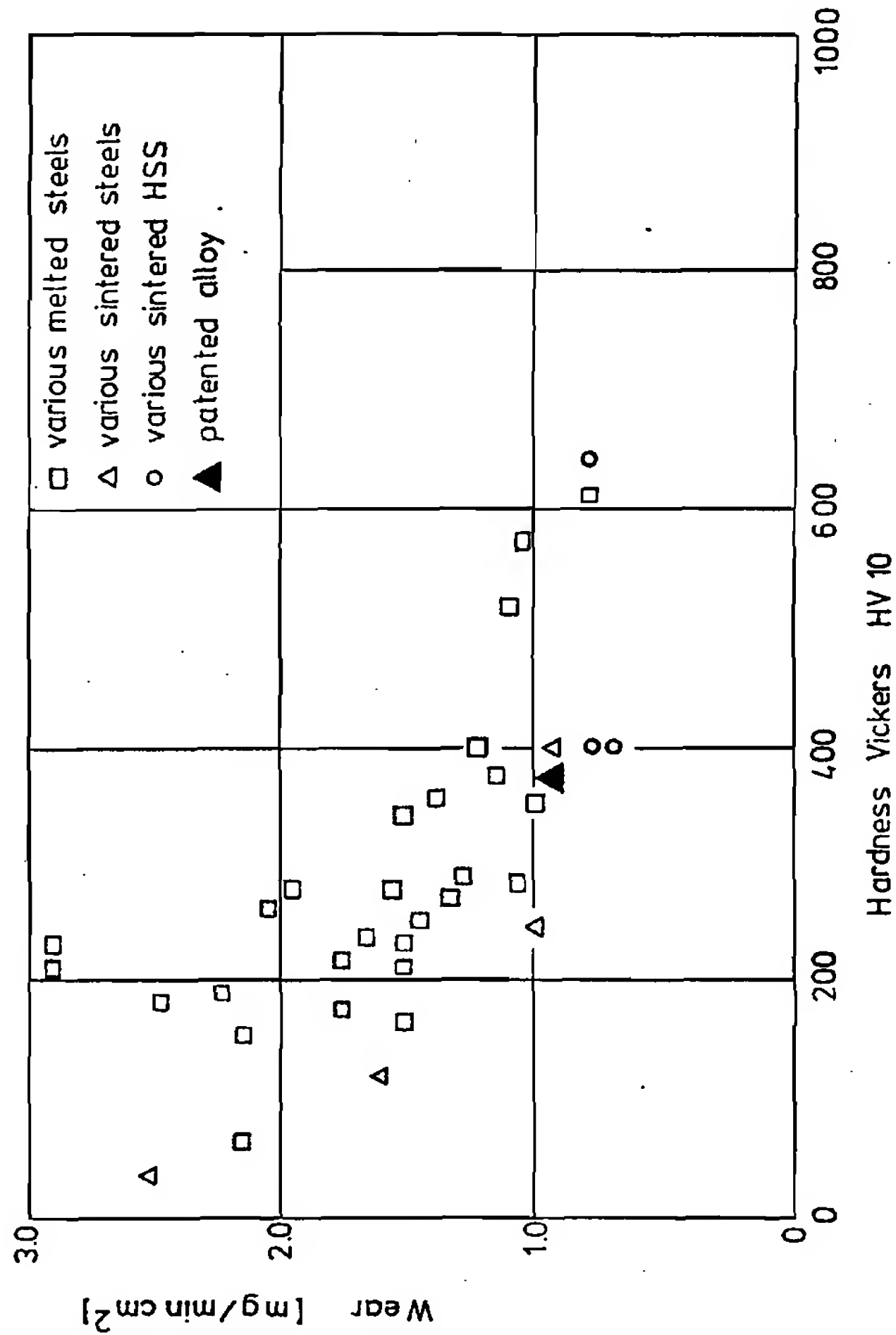


FIG. 5